



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: : Docket No: Q80752
Kazuyoshi Mizutani, et al. : Group Art Unit: 1752
Appln. No.: 10/812,092 : Examiner: Cynthia Hamilton
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For: POSITIVE RESIST COMPOSITION

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents
Alexandria, VA 22313-1450

Sir:

I, Kazuyoshi Mizutani, do declare and state as follows:

I am a citizen of Japan.

I graduated from Graduate School of Osaka University in the course of chemistry in March 1988, attaining a Master's degree.

Since April 1988, I have been employed by Fuji Photo Film Co., Ltd. and have been engaged in development of photosensitive materials for positive-working printing plate, development of anti-reflective film materials for photoresist, development of photosensitive Si polymer materials for two layers-resist, and development of materials for electron beam resist.

I am a co-inventor of the invention described and claimed in the above-named application, and I am familiar with the subject matter disclosed by the application.

In order to demonstrate the unexpected superiority of the present invention, the following experimentation was conducted.

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EXPERIMENTATION

The Applicants repeated the Examples of JP 2002-49156 (JP '156) as indicated below.

Repeated experiment of Synthesis example 1 (synthesis of polymer having phenolic-hydroxyl group: resin R-1):

32.4 g (0.2 mol) of p-acetoxystyrene were dissolved in 120 ml of methanol, and agitated under a nitrogen flow, then 0.033 g of azobisisobutyronitrile (AIBN) were added at 60 °C and a polymerization was conducted by continuing agitation for 12 hours. After the reaction, dilute hydrochloric acid was added to the reaction mixture to cleave the acetoxy group, and volatile components were distilled off by a distillation under a reduced pressure. An obtained resin was re-dissolved in 150 ml of methanol, and added to a large amount of water to obtain white polymer. An operation of re-dissolving the polymer in methanol and adding to a large amount of water was repeated three times, then the obtained resin was dried for 24 hours at 60°C in a vacuum drier to obtain poly(p-hydroxystyrene) (resin R-1). The obtained resin had a weight average molecular weight of 15,200 and a molecular weight dispersion degree of 1.95.

Repeated experiment of Synthesis example 2 (synthesis of polymer having phenolic hydroxyl group: resin R-2):

35.25 g (0.2 mol) of p-tert-butoxystyrene monomer, purified by dehydration and distillation according to an ordinary method, and 2.42 g (0.0151 mol) of p-tert-butylstyrene were dissolved in 100 ml of tetrahydrofuran. In a nitrogen flow and under agitation, 0.033 g of azobisisobutyronitrile (AIBN) were added, at

83°C, three times every 3 hours, and the agitation was continued for further 6 hours to execute a polymerization reaction. The reaction liquid was charged in 1200 ml of hexane to precipitate a white resin. The obtained resin was dissolved, after drying, in 150 ml of tetrahydrofuran. The solution was added with 4N hydrochloric acid, and refluxed under heating for 6 hours to execute a hydrolysis, and re-precipitated in 5 L of deionized water. The resin was separated by filtration, rinsed with water and dried. It was again dissolved in 200 ml of tetrahydrofuran, and dropwise added to 5 L of deionized water under vigorous agitation to execute a re-precipitation. This re-reprecipitation was repeated three times. The obtained resin was dried for 24 hours at 60°C in a vacuum drier, thereby obtaining a poly(p-hydroxystyrene/p-tert-butylstyrene)copolymer (resin R-2). The obtained resin had a weight average molecular weight of 10,500 and a molecular weight dispersion degree of 1.90.

Repeated experiment of Synthesis example 3 (synthesis of polymer having phenolic hydroxyl group: resin R-3):

40 g (0.33 mol) of p-hydroxystyrene, and 10.7 g (0.08 mol) of tert-butyl acrylate were dissolved in 50 g of dioxane, then 8 g of azobisisobutyronitrile (AIBN) were added therein and the mixture was agitated for 8 hours under heating at 60°C in a nitrogen flow. The reaction liquid was charged in 1200 ml of hexane to precipitate a white resin. The obtained resin after drying was dissolved in acetone and dropwise added to 5 L of deionized water under vigorous agitation to execute re-precipitation. This re-precipitating operation was repeated three times. The obtained resin was dried for 24 hours at 60°C in a vacuum drier, thereby obtaining a poly(p-hydroxystyrene/tert-butyl acrylate) copolymer (resin R-3). The obtained resin had a weight average molecular weight of 21,000 and a

molecular weight dispersion degree of 2.15.

Synthesis example 4 (synthesis of acid decomposable polymer (a): polymer B-1):

50 g of poly(p-hydroxystyrene) (resin R-4) manufactured by Nippon Soda Co. (molecular weight: 10,000, dispersion degree: 1.85) were dissolved in 240 g of propylene glycol monomethyl ether acetate (PGMEA), and this solution was heated to 60°C at a reduced pressure of 20 mmHg to remove about 40 g of solvent together with the water remaining in the system. After cooling to 20°C, 6.1 g of ethyl vinyl ether, 4.0 g of separately synthesized cyclohexyl phenoxyethylvinyl ether and 0.02 g of paratoluenesulfonic acid were added and the mixture was agitated for 1 hour at the room temperature. Then the mixture was neutralized by adding 0.02 g of triethylamine, and an extraction with 240 g of ethyl acetate and 140 g of water was conducted three times. There was obtained a polymer B-1. The obtained resin had a weight average molecular weight of 11,000 and a molecular weight dispersion degree of 1.95.

Synthesis examples 5 - 13 (synthesis of acid decomposable polymers (a): polymers B-2 - B-10):

Acid decomposable polymers were synthesized in the same manner as in Synthesis example 4 except for employing a polymer having a phenolic hydroxyl group (base polymer) and two alkyl vinyl ethers shown in Table 1 of JP '156 to obtain polymers B-2 - B-10. Also a comparative resin (C-1) was synthesized in the same manner except for employing only one alkyl vinyl ether described in Table 1 of JP '156. Also the obtained polymers were subjected to an evaluation according to the examples in the present specification. The weight average

molecular weight, the molecular weight dispersion degree and results of evaluation are summarized in the following Table A.

Table A

Repeated experiment of JP'156 (Comp. ex.)	Molecular weight	Molecular weight dispersion degree	In-vacuo PED	
			Line width change (nm)	LER
B-1 (I')	11000	1.95	1.8	8.1 → 8.5
B-2 (II')	16000	2.05	1.9	8.3 → 8.6
B-3 (III')	23000	2.20	1.8	8.4 → 8.8
B-4 (IV')	11500	2.20	1.9	8.1 → 8.6
B-5 (V')	15800	2.10	1.8	8.2 → 8.6
B-6 (VI')	24200	2.35	1.9	8.3 → 8.8
B-7 (VII')	11500	1.95	1.9	8.2 → 8.5
B-8 (VIII')	11200	2.00	1.8	8.9 → 9.2
B-9 (IX')	12400	1.95	1.8	8.7 → 9.0
B-10 (X')	13000	2.05	1.9	8.7 → 9.1

In the following, Examples of the present specification are described again, clarifying the molecular weight dispersion degree.

R-1: It was obtained from Nippon Soda as a mono-dispersed resin synthesized by an anionic polymerization. The resin had a weight average molecular weight of 8000 and a molecular weight dispersion degree of 1.05.

Resin R-2 (synthesis of polymer having phenolic hydroxyl group: resin R-2):

32.4 g (0.2 mol) of p-acetoxystyrene were dissolved in 120 ml of toluene, and 0.04 g of TEMPO (manufactured by Tokyo Kasei Kogyo Co.) were added

therein. The mixture was agitated under a nitrogen flow, then 0.063 g of azobisisobutyronitrile (AIBN) were added at 120°C and a polymerization was conducted by continuing agitation for 12 hours. After the reaction, dilute hydrochloric acid was added to the reaction mixture to partially cleave the acetoxy group, and volatile components were distilled off by a distillation under a reduced pressure. An obtained resin was re-dissolved in 150 ml of methanol, and added to a large amount of water to obtain white polymer. An operation of re-dissolving the polymer in methanol and adding to a large amount of water was repeated three times, then the obtained resin was dried for 24 hours at 60°C in a vacuum drier to obtain poly(p-hydroxystyrene) (resin R-2). The obtained resin had a weight average molecular weight of 9,000 and a molecular weight dispersion degree of 1.4.

Resin R-3 (synthesis of polymer having phenolic hydroxyl group: resin R-3)

40 g (0.33 mol) of p-hydroxystyrene, and 10.7 g (0.08 mol) of tert-butyl acrylate were dissolved in 50 g of toluene, and 0.04 g of TEMPO were added therein. Then 8 g of azobisisobutyronitrile (AIBN) were added and the mixture was agitated for 8 hours at 105°C in a nitrogen flow. The reaction liquid was charged in 1200 ml of hexane to precipitate a white resin. The obtained resin after drying was dissolved in acetone and dropwise added to 5 L of deionized water under vigorous agitation to execute re-precipitation. This re-precipitating operation was repeated three times. The obtained resin was dried for 24 hours at 60°C in a vacuum drier, thereby obtaining a poly(p-hydroxystyrene/tert-butyl acrylate)copolymer (resin R-3). The obtained resin had a weight-average molecular weight of 10,000 and a molecular weight dispersion degree of 1.5.

Resin R-4 (synthesis of polymer having phenolic hydroxyl group: resin R-4):

35.25 g (0.2 mol) of p-tert-butoxystyrene monomer, purified by dehydration and distillation according to an ordinary method, and 4.6 g (0.04 mol) of styrene were dissolved in 100 ml of toluene. After adding 0.04 g of TEMPO, 0.10 g of azobisisobutyronitrile (AIBN) were added at 110°C in a nitrogen flow and under agitation, and the agitation was continued for further 6 hours to execute a polymerization reaction. The reaction liquid was charged in 1200 ml of hexane to precipitate a white resin. The obtained resin was dissolved, after drying, in 150 ml of tetrahydrofuran. The solution was added with 4N hydrochloric acid, and refluxed under heating for 6 hours to execute a hydrolysis, and re-precipitated in 5 L of deionized water. The resin was separated by filtration, rinsed with water and dried. It was again dissolved in 200 ml of tetrahydrofuran, and dropwise added to 5 L of deionized water under vigorous agitation to execute a re-precipitation. This re-precipitation was repeated three times. The obtained resin was dried for 24 hours at 60°C in a vacuum drier, thereby obtaining a poly(p-hydroxystyrene/p-tert-butylstyrene)copolymer (resin R-4). The obtained resin had a weight average molecular weight of 10,000 and a molecular weight dispersion degree of 1.5.

The above-described resins R-1 to R-4 were employed for synthesizing resins B-1 to B-9 of the present invention. Following Table B shows results of the examples of the present invention, corresponding to the Examples of the cited document (with same combinations of acetal protecting groups). (Evaluation method being same as described in the present specification)

Table B

The present invention (Examples)	Molecular weight	Molecular weight dispersion degree	In-vacuo PED	
			Line width change (nm)	LER
B-1 (I)	9500	1.10	1.6	6.1 → 6.2
B-2 (II)	9700	1.15	1.7	6.4 → 6.5
B-3 (III)	11000	1.48	1.6	6.3 → 6.4
B-4 (IV)	11500	1.50	1.7	6.4 → 6.5
B-5 (V)	9500	1.20	1.6	6.7 → 6.9
B-6 (VI)	10500	1.50	1.7	6.5 → 6.6
B-7 (VII)	11000	1.48	1.6	6.7 → 6.8
B-8 (VIII)	11200	1.50	1.7	6.4 → 6.6
B-9 (IX)	12400	1.50	1.7	6.6 → 6.8

As will be apparent from the Comparative Examples I' - X', examples of JP'156 executed specifically do not have the molecular weight dispersion degree of the present invention.

Also the comparison of the Comparative Examples I' - IX' with the Examples I - IX clearly indicates the feature of the present invention of exhibiting unexpected specific effects in vacuo PED (Line width change and LER) by having a polymer of a specified structure with a specified molecular weight dispersion degree.

Such effects are specific effects in the resist composition of the present invention for forming an image by an irradiation with an electron beam, an X-ray or an EUV, and are not disclosed nor suggested specifically in the cited reference.

Even if the cited reference includes a general description on the dispersion degree, heat resistance and image characteristics, it is not considered to teach

the specific means of the present invention for solving the particular problem required in a resist composition for forming an image by an irradiation with an electron beam, an X-ray or an EUV.

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Date: 1 / 11 / 2006

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